FY95 Fnd of Fiscal Year Letter
(01 Oct 1994 - 30 Sept 1995)

ONR CONTRACT INFORMATION

Contract Title: HIGH THERMAL CONDUCTIVITY FIBERS FROM PBO

Performing Organization: Clemson University

Principal Investigator: Dan D. Edie
[Ph.(803)656-3056, FAX (803)656-0784]

Contract Number: N00014-94-1-1159 (CU REF:05-5911)

R & T Project Number: ccassrt---01

ONR Scientific Officer: A. K. Vasudevan

REPORT DOCUMENTATION PAGE

FORM APPROVED
OMB No. 0704-0188

1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED
	18 Nov 95	End of Fiscal Year Letter 1 Oct 94 - 30 Sep 95

4. TITLE AND SUBTITLE OF REPORT
High Thermal Conductivity Fibers from PBO

5. FUNDING NUMBERS
N00014-94-1-1159

6. AUTHOR(S)
Dr. Dan D. Edie

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
Clemson University
Box 340903; 123 Earle Hall
Chemical Engineering
Clemson, SC 29634-0909

8. PERFORMING ORGANIZATION REPORT NUMBER:
05-5911

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
Office of Naval Research
ONR 252 DG
Ballston Tower One
800 North Quincy Street
Arlington, VA 22217-5660

10. SPONSORING/MONITORING AGENCY REPORT NUMBER:

19960521 000

11. SUPPLEMENTARY NOTES:

12a. DISTRIBUTION AVAILABILITY STATEMENT
Unlimited

12b. DISTRIBUTION CODE

13. ABSTRACT (Maximum 200 words)

The objective of this project is to examine the conversion of poly p-phenylenebenzobisoxazole (PBO) to carbon fiber. The production of polymer-based carbon fibers usually involves heating the precursor fiber to approximately 300 °C to crosslink the polymeric structure, thus rendering it infusible, and then heating the crosslinked fiber to much higher temperatures to drive off most non-carbon elements. Because stabilization occurs as a separate step, establishing its influence on the structure and properties of the final carbon fiber is relatively straightforward. A series of three stabilization trials were performed, and then all three stabilized fiber samples were heated to 2000 °C at 20 °C per minute. A carbonized length of as-received PBO fiber served as a control. The results showed that stabilization did not improve the tensile characteristics of the final carbon fiber. In Dow's production of PBO fiber, the fiber is heat treated to a temperature of 550 °C for 10-30 seconds. This additional heat treatment reduced the fiber's tensile strength, but increased its modulus and compressive strength. Future research will be conducted upon the carbonized fiber to determine its thermal conductivity, crystallinity and orientation, and the kinetics of the carbonization process.

14. SUBJECT TERMS	15. NUMBER OF PAGES: 6
	16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT:	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
Unclassified	Unclassified	Unclassified	

A. Research Goals

The objective of the project is to examine the conversion of poly p-phenylenebenzobisoxazole (PBO) to carbon fiber. The aromatic, rigid-rod backbone of the polymer enables the carbonized fiber to develop a three-dimensionally ordered structure without stabilization. Because of this structure, PBO fibers appear capable of developing relatively high thermal conductivities when carbonized.

B. Significant Results

The production of polymer-based carbon fibers usually involves heating the precursor fiber to approximately 300°C in air to crosslink the polymeric structure, rendering it infusible, and then heating the crosslinked fiber to much higher temperatures (from 2000 to 3000°C) to drive off most non-carbon elements. During this first year of the project, studies of the various stages of this conversion process for PBO precursor fibers were initiated. Developing a fundamental understanding of the PBO-carbon fiber conversion process is the goal of this effort.

Because stabilization occurs as a separate step in the conversion process, establishing its impact on the structure and properties of the final carbon fiber is relatively straightforward. Thus, study during first year focused on determining the effect of this initial process step. High temperature heat treatment involves three distinct stages (precarbonization, carbonization, and graphitization). The effect of these three stages on the conversion of PBO to carbon fiber will be investigated during the next two years of the project.

During oxidative stabilization, oxygen creates crosslinks between the polymer chains within the PBO fiber. This oxygen must come from either the precursor and/or the surrounding air. Therefore, fiber mass gain is used as a measure of the effectiveness of fiber stabilization in air. To test the oxygen uptake of PBO fibers, 2.5 milligrams of PBO fiber were heated in a TGA pan under air from room temperature to 800 °C. As Figure 1 indicates, no detectable mass gain occurred. This indicates that the oxygen from the air is not retained by the PBO fiber. Thus, stabilization in air would not result in the increased oxygen crosslinking commonly observed in other polymers such as PAN.

A series of three stabilization trials were performed. Each of the three samples was heated at a rate of 5 °C per minute to 310 °C and held at that temperature for 30, 60, and 120 minutes, respectively. Finally, all three stabilized fiber samples were subsequently heated to 2000 °C at a rate of 20 °C per minute. A length of as-received PBO fiber also was carbonized and served as a control.

Final results showed that stabilization did not enhance the tensile properties of the final carbon fiber. Neither tensile strength nor modulus improved with stabilization, regardless of the stabilization dwell time. This indicates that the expensive and time-consuming stabilization step may be completely eliminated from the carbonization process without adversely influencing the properties of the fiber.

In Dow's pilot-scale PBO process, the fiber is heat treated to a temperature of 550 °C for 10-30 seconds in order to enhance its crystallinity and modulus. However, our initial research indicates that the balance of properties can be altered substantially by additional heating below 540 °C. The fiber was heated under argon to a temperature of 530 °C and maintained for fifteen minutes, before

the fiber was allowed to cool to room temperature. As Table 1 shows, this additional heat treatment reduced the fiber's tensile strength and increased its modulus. More importantly, the additional low temperature treatment substantially increased the fiber's compressive strength.

C. Future Research

The precarbonized heat-treated PBO fibers will be carbonized and their thermal conductivity will be measured. The crystallinity and orientation of the carbonized fibers will also be examined to determine the graphitizability of PBO. In addition, the kinetics of the carbonization process will be modeled.

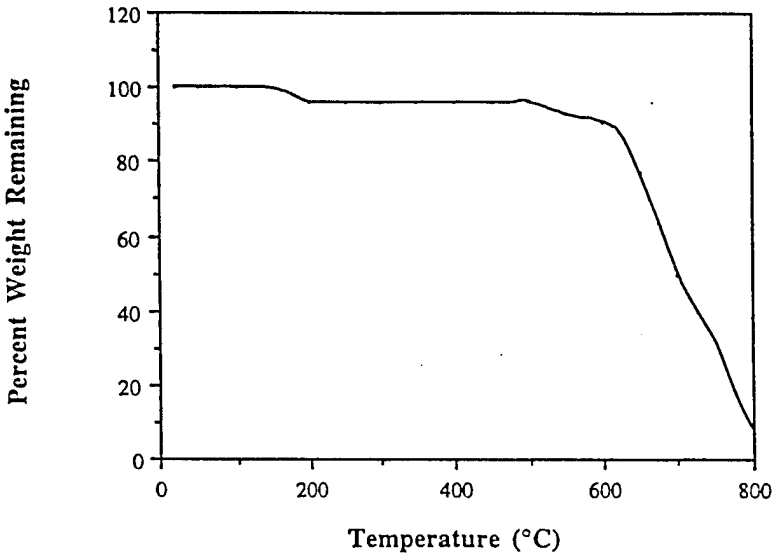

Figure 1. Thermogravimetric analysis profile of PBO fibers in air.

Table 1. Mechanical Properties of PBO Fibers Before and After Heating.

Property	As-Received	Heat Treated
Tensile Strength (MPa)	4130	2700
Tensile Modulus (GPa)	146	211
Compressive Strength (MPa)	380	620
Color	Yellow	Red
Crystallite Size (nm)	32	36

D. List of Publications/Reports/Presentations

1. Papers Published in Refereed Journals

"Direct Carbonization of PBO Fiber," J. A. Newell, D. K. Rogers, D. D. Edie and C. C. Fain, *Carbon*, **32** (4), pp. 651-658, 1994.

"Factors Limiting the Tensile Strength of PBO-Based Carbon Fibers," J. A. Newell and D. D. Edie, *Carbon*, in press.

2. Non-Refereed Publications and Published Technical Reports

3. Presentations
a. Invited

b. Contributed

"Factors Limiting the Tensile Strength of PBO-Based Carbon Fibers," J. A. Newell and D. D. Edie, 1994 AIChE Annual Meeting, San Francisco, CA November 13-18, 1994.

4. Books (and sections thereof)

E. LIST OF HONORS/AWARDS

Name of Person Receiving Award	Recipient's Institution	Name, Sponsor and Purpose of Award
Dan D. Edie	Clemson University	Elected to the Executive Council of the American Carbon Society

F. Participants

James Newell, completed Ph.D. in Chemical Engineering and graduated from Clemson University in December, 1994.

Chad Mundt, Ph. D. student currently enrolled in Chemical Engineering at Clemson University.

Both of the above are U. S. citizens

G. Other Sponsored Research During Grant Period

This Grant

"High Thermal Conductivity Fibers from PBO," Sponsored by ONR, 0% of time, $91,176/yr, 7/31/94 to 8/1/97.

Other Grants

"High Thermal Conductivity Fibers," Sponsored by the Great Lakes Composite Consortium, $220,000/yr, 30% of time, 1/1/92 to 12/31/95.

"High Thermal Conductivity Carbon/Carbon Composites," Office of Naval Research, $31,100/yr, 0% of time, 10/1/92 to 9/31/95.

"Production of Carbon Monofilament- Phase II," Sponsored by MSNW, $150,000/yr, 5% of time, 3/3/95 to 5/3/96.

"Supercritical Extraction for High Thermal Conductivity Fibers," Sponsored by DEPSCoR, $100,000/yr, 15% of time, 9/1/94 to 8/31/97.

"Engineering Fibers and the Micromechanics of Their Composites," Sponsored by NSF, $95,000/yr, 17% of time, 7/1/92 to 6/31/95.